Thermocapillary-assisted pulling of thin films

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We study the thermocapillary stabilization of a free liquid film as it is formed by being pulled out of a bath at constant speed. For sufficiently large stresses induced at the interface through a controlled temperature gradient, a continuous film of liquid can be processed. For negligible inertial effects, the film thickness only depends on the capillary length and on the strength of the surface tension variation. The theory suggests that very thin ribbons or foils of molten material can be drawn out of a melt over a wide range of thicknesses and at speeds relevant to manufacturing.

Many objects used everyday are made of metallic foils, the most obvious example being aluminum foil. An ancestral process to produce foils is by rolling[1], which is a forming process where metal stock is passed through a pair of rolls. Another technique is the foil-casting process, used for instance to produce silicon foils[2]. The method consists of depositing a liquid metal on a moving and subcooled substrate through the bottom of a casting frame, so that a layer of the liquid metal crystallizes on the substrate, and a metal foil is formed[3]. Both foil rolling and casting methods place the liquid metal in contact, at least on one side, with a solid substrate, which is undesirable for production of extremely pure and flat materials.

Silicon sheets produced by vertical growth from a melt are contact-free but the production speed is much smaller than the aforementioned techniques[4]: the speed is typically limited to a few mm/s to avoid breaking the liquid bridge between the melt and the foil. In fact, no stable film can be pulled out of a liquid bath if only extensional viscous and capillary forces are in balance[5]. Nevertheless, soap films can be formed at large speeds (m/s) due to interfacial stresses induced by the presence of surfactant concentration gradients at the free surfaces[6]. Surfactant can obviously not be used to produce foils of pure materials but interfacial thermocapillary stresses could be used instead by prescribing temperature gradients along the free surfaces.

The concept of stabilizing the formation of free liquid films by thermocapillary effects has not been reported previously. The ideas should be applicable to the production of contact-free foils at competitive speeds, and here we focus on the fluid dynamics aspects of this concept.

We consider a liquid film withdrawn with speed u_0 from a bath of temperature T_b (Fig. 1). Symmetry is assumed about the x-axis. The prescribed far-field ambient temperature is denoted $T_a(x)$. At steady state, a film of thickness $h(x)$ eventually reaches a constant value h_0 at a distance sufficiently far above the bath. We assume the film then solidifies. The density ρ and the viscosity
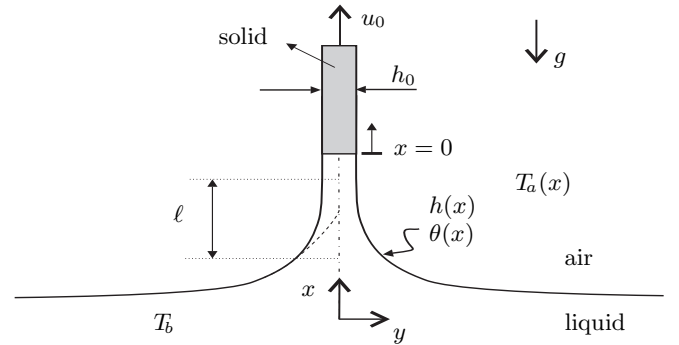

FIG. 1. Sketch of the pulling film problem. The dashed line indicates a static meniscus (not to scale).

η are taken to be constant because they do not change significantly over a modest temperature interval near the solidification temperatures of typical materials that interest us. We denote $\theta(x)$ as the cross-sectional average temperature of the film and assume a linear decrease of the surface tension γ with temperature from the solidification temperature T_s, $\gamma(\theta) = \gamma_s - \gamma_T(\theta - T_s)$, where $\gamma_s = \gamma(T_s)$ and $\gamma_T = |\mathrm{d}\gamma/\mathrm{d}T|$, as is the case for most liquid metals[7].

Following the region decomposition applied in the context of a foam lamella[8], determination of the shape of the film requires solving the thin-film equation in an intermediate region of length ℓ that connects the static meniscus at the bath with the flat film region near the solidification front. The static meniscus (dashed line in Fig. 1) is identical to a meniscus that would be attached to a perfectly wetting substrate with curvature $h'' = \sqrt{2}/\ell_c$, where the prime denotes the x-derivative, and $\ell_c = \sqrt{\gamma_s/(\rho g)}$ is the capillary length[9]. Because of the downward capillary suction induced by the positive curvature of the free surface, no purely viscous film can be stably pulled out of a liquid bath[5] unless sufficiently large shear stress is present at the free surface, which is ensured here by the Marangoni stress induced by the gradients of surface temperature on

both sides of the film. According to Breward and Howell[8] this "shear flow" regime corresponds to a distinguished limit where capillary and Marangoni effects provide the dominant balance in the intermediate region and where the extensional viscous stress is always negligible. This limit is applicable for

$$Ca = \frac{\eta u_0}{\gamma_s} = O(\varepsilon^3) \quad \text{and} \quad Ma = \frac{\gamma_T \Delta T}{\eta u_0} = O(\varepsilon^{-1}) \,, \tag{1}$$

with $\varepsilon = h_0/\ell$ and $\Delta T = T_b - T_s$. The corresponding axial stress equation, neglecting inertia and gravity effects (see justifications hereafter), has the form

$$\frac{\gamma_s}{2} h h''' - 2\gamma_T \theta' = 0 \,. \tag{2}$$

Terms in (2) account, respectively, for the capillary stress induced by the curvature of the interface and for the thermocapillary stresses at the two interfaces. Finally, in the case where the rate of heat transfer across the free surfaces is much larger than the rate of heat advected by the flow, the local temperature of the film takes the temperature of the ambient (the reader is referred to Scheid *et al.*[10] for details on this 'prescribed temperature limit'), such that the energy equation reduces to

$$\theta(x) \approx T_a(x) \,. \tag{3}$$

We also assume that heat released during solidification can be neglected because it occurs after the geometry of the film is no longer changing[11]. In the present problem, we assume the ambient temperature to be prescribed such that it varies by the temperature difference ΔT over a distance d. For the sake of subsequent analytical development, we chose a continuous and integrable function of the form

$$T_a(x) = T_s + \frac{\Delta T}{2} \left(1 - \tanh \left[2\pi \left(\frac{x}{d} + 1 \right) \right] \right) \,. \tag{4}$$

We note that the choice of a function other than an hyperbolic tangent (such as an error function for instance) leads to the same conclusions as those presented in this letter. Because the problem is invariant by translation, and according to the sketch in Fig. 1, we have also shifted in space the temperature variation by the quantity d such that $T_a(0) \approx T_s$. This is valid so long as $\Delta T/T_s \ll 1$.

We next nondimensionalize using the scalings

$$X = \frac{x}{\ell}, \quad D = \frac{d}{\ell}, \quad H = \frac{h}{h_0}, \quad \Theta = \frac{\theta - T_s}{\Delta T} \,. \tag{5}$$

Defining the length scale ℓ of the intermediate region as

$$\ell = \frac{h_0}{2\sqrt{\Gamma}} \quad \text{with} \quad \Gamma = \frac{\gamma_T \Delta T}{\gamma_s} \,, \tag{6}$$

leads to the parameterless equation

$$HH''' = \Theta' \,. \tag{7}$$
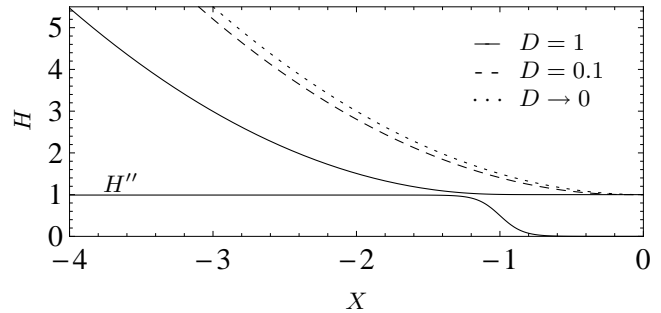

FIG. 2. Solutions to (8) showing H for various D and H'' for $D = 1$. The dotted line also corresponds to $H = 1 + X^2/2$.

Since the thickness is assumed to reach a constant near the solidification front, the boundary conditions at $X = 0$ are $H = 1$ and $H' = H'' = \Theta = 0$. Integrating (7) and combining with (3) and (4) in dimensionless form, yields

$$2HH'' - H'^2 = 1 - \tanh \left[2\pi \left(\frac{X}{D} + 1 \right) \right] \,, \tag{8}$$

which straightforwardly relates the dimensionless length of the temperature (or interfacial stress) variation D to the shape of the film $H(X)$. Furthermore, this latter must match the curvature of the static meniscus as the film thickens, i.e. $H''_{-\infty} = \sqrt{2}\,\ell^2/(\ell_c h_0)$ as $X \to -\infty$. Therefore, the matching condition that allows determination of h_0, using (6), yields

$$h_0 = 2\sqrt{2}\,\ell_c\, H''_{-\infty}\,\Gamma \,, \tag{9}$$

where $H''_{-\infty}$ remains to be determined.

In the limit $D \to 0$ and for $X < 0$, the term $\tanh \to -1$ in (8) so that an analytical solution can be found: $H = 1 + X^2/2$. Replacing the corresponding curvature $H''_{-\infty} = 1$ in the matching condition (9) yields the asymptotic determination of the film thickness:

$$h_0 = 2\sqrt{2}\,\ell_c\,\Gamma \quad \text{as} \quad D \to 0 \,. \tag{10}$$

This prediction for the typical film thickness is the main result of this work showing that it only depends on the amplitude of the surface tension variation, as measured by the parameter Γ. The film is thus pulled out of the intermediate region with a thickness that does not depend on the pulling speed. Increasing the speed will thus increase the rate of liquid passing through this 'virtual 'slot', whose the width is adjusted by the amplitude of the thermocapillary stresses. As the pulling speed increases, however, eventually inertial effects will enter the axial stress balance (2), and we comment on this influence below.

Equation (8) can be solved numerically for any value of D; typical solutions are given in Fig. 2. We observe that even though the numerical solution for $D = 1$ is far from the analytical $D \to 0$ solution (contrary to the $D = 0.1$ solution), the curvature H'' still tends to a constant approaching unity as $X \to -\infty$.
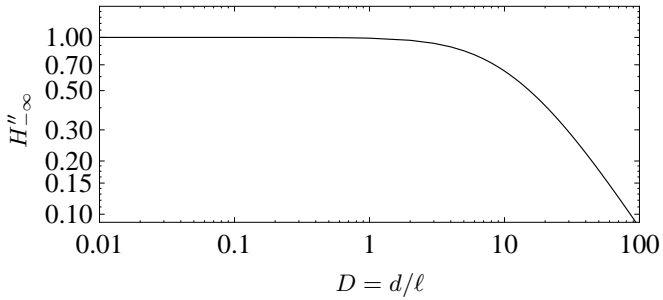
FIG. 3. Matching curvature $H''_{-\infty}$ versus the length D over which the temperature difference is applied.

TABLE I. Properties given at the solidification temperature T_s for various elements[a]; $\ell_c = \sqrt{\gamma_s/(\rho g)}$ and $\Delta T = 100$K.

		Ag	Al	Au	Co	Cu	Fe	Ni	Si
T_s	K	1235	933	1337	1773	1357	1811	1727	1683
ρ	kg/m^3	9150	2350	17400	7810	7900	7040	7920	2520
γ_s	N/m	0.91	0.88	1.12	1.89	1.29	1.92	1.77	0.78
γ_T	mN/m/K	0.18	0.20	0.09	0.33	0.23	0.40	0.33	0.65
ℓ_c	mm	3.2	6.2	2.6	5.0	4.1	5.3	4.8	5.6
Γ	$\gamma_T\Delta T/\gamma_s$	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.08

[a] I. Egry and J. Brillo, J. Chem. Eng. Data **54**, 2347 (2009).

We next report in Fig. 3 the constant value $H''_{-\infty}$ for a wide range of D. It appears that $H''_{-\infty}$ is well approximated by unity for $D \lesssim 1$, which extends the range of validity of the asymptotic result (10). However, for $D > 1$, numerical solutions in Fig. 3 should be used instead for $H''_{-\infty}$, which gives the film thickness by (9). The results show that the film thickness h_0 decreases as D increases, i.e. as the imposed temperature gradient decreases.

Table I shows the physical properties of various metallic elements, which allows an assessment of the dimensionless parameter Γ for a fixed value of the temperature difference $\Delta T = 100$ K. We see that $\Gamma \approx 10^{-2}$ for all of the elements reported in Table I, except for silicon which has a higher value. However, Zhou *et al.*[12] report smaller values of $\gamma_s = 0.72$ N/m and $\gamma_T = 0.06$ mN/(m K) for silicon, which gives $\Gamma = 0.01$. The film thickness is therefore of the order of 100 μm for all of the elements in Table I.

Taking a practical example, to produce an iron film of 150 μm thick would require a value of $\Gamma = 0.01$, or a variation of surface tension by 20 mN/m over a length smaller than or about $\ell = \ell_c\sqrt{2\Gamma}$ as found from Eq. (6) with the asymptotic result (10). This case requires lowering the temperature of the surface of the film by 50 K over a distance smaller than or about 0.8 mm (i.e. $D \lesssim 1$). If the temperature difference is to be imposed over a longer distance, the numerical results in Fig. 3 are to be used with (9). For instance, for $D = 10$, it is necessary to increase Γ by 60% to keep the same film thickness as that obtained for $D \lesssim 1$; in the case of a 150 μm thick iron foil, this approach requires a temperature difference of 80 K over a distance of about 6 mm.

We now determine the conditions that allow neglect of gravity and inertia: both of them remain small as compared to capillary effects, so long as $G = \rho g \ell_c^2/\gamma_s \ll 1$ and $We = \rho \ell_c u_0^2/\gamma_s \ll 1$, respectively. Note the largest length scale of the system, ℓ_c, has been taken to ensure a conservative evaluation of G and We. For typical molten materials, the first condition is always true since $G \approx 10^{-1}$ for all of the elements in Table I. The second condition indicates that inertial effects can be neglected for speeds $u_0 \ll \sqrt{g\ell_c}$. In the case of a 150 μm iron foil, we require $u_0 \ll 22$ cm/s. For larger speeds, inertia will tend to thin the film as compared to the present theory. Detailed analysis including inertia is to be reported elsewhere.

As mentioned earlier, the present results are applicable in the 'shear' distinguished limit where thermocapillary stresses are large and extensional viscous stresses are negligible. Using (1) together with (6) and (10) gives a condition on the pulling speed, $u_0 \lesssim (\gamma_s/\eta)\,\Gamma^{3/2}$, or in the case of iron with $\eta \approx 10^{-3}$ Pa.s, $u_0 \lesssim 1$ m/s.

In this letter, we show that a liquid film can be pulled out of a bath by using thermocapillary stresses prescribed at the free surfaces. The resulting film thickness is proportional to the capillary length of the liquid ℓ_c and to a parameter Γ that measures the amplitude of the surface tension change at the interface. If this change is imposed over a distance d that is larger than the characteristic length $\ell = \ell_c\sqrt{2\Gamma}$ of the system, the film thickness decreases with increasing d, otherwise it is independent of d. A significant feature of the present theory is that the film thickness is also independent of the pulling speed of the film, at least when inertia is neglected, which means that the flow rate can be changed without modifying the film thickness.

[1] E. P. Degarmo, J. T. Black, and R. A. Kohser, *Materials and Processes in Manufacturing* (Wiley, New York, 2003), 9th ed.

[2] D. Helmreich and E. Sirtl, J. Cryst. Growth **79**, 562 (1986).

[3] A. G. Schoenecker and K. I. Steinbach, *Method and device for producing metal foils*, Patent EP1743385(B1) (2008).

[4] J. D. Zook and S. B. Schuldt, J. Cryst. Growth **50**, 51 (1980).

[5] E. A. van Nierop, B. Scheid, and H. A. Stone, J. Fluid Mech. **602**, 119 (2008), Corrigendum: **630**, 443 (2009).

[6] K. J. Mysels, K. Shinoda, and S. Frankel, *Soap Films: Studies of Their Thinning* (Pergamon, London, 1959).

[7] H. M. Lu and Q. Jiang, J. Phys. Chem. B **109**, 15463 (2005).

[8] C. J. Breward and P. D. Howell, J. Fluid Mech. **458**, 379 (2002).

[9] P.-G. de Gennes, F. Brochart-Wyart, and D. Quéré, *Gouttes, Bulles, Perles et Ondes* (Belin (Paris), 2005).

[10] B. Scheid, S. Quiligotti, B. Tran, R. Gy, and H. A. Stone, J. Fluid Mech. **636**, 155 (2009).

[11] S. Smith and D. Stolle, Polym. Eng. Sc. **40**, 1870 (2000).

[12] Z. Zhou, S. Mukherjee, and A.-K. Rhim, J. Cryst. Growth **257**, 350 (2003).